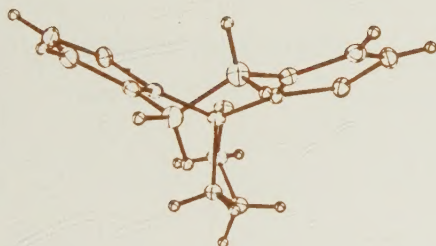


**CRYSTALLOGRAPHIC STUDIES OF SOME BORORGANIC
AND RELATED COMPOUNDS IN THE SOLID STATE**

IRENA CYNKIER



Lund 1981



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***CRYSTALLOGRAPHIC STUDIES OF SOME BORORGANIC
AND RELATED COMPOUNDS IN THE SOLID STATE***

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SWEDEN

LUND 1981

CRYSTALLOGRAPHIC STUDIES OF SOME ORGANIC
AND RELATED COMPOUNDS IN THE SOLID STATE

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Leiden



1981

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Title and subtitle CRYSTALLOGRAPHIC STUDIES OF SOME BORORGANIC AND RELATED COMPOUNDS IN THE SOLID STATE			
Abstract Crystal structures of some <u>bororganic compounds</u> and two <u>dithienotropones</u> have been determined by <u>X-ray diffraction techniques</u>. The substances investigated include compounds with three- and four-coordinated boron. Several have a <u>spiro oxazaborolidine ring</u>. Most of them have <u>tricyclic fused ring systems</u> with a central <u>seven-membered ring</u> and either thiophene or benzene side rings. <u>Packing</u>, <u>planarity</u> and <u>aromaticity</u> were studied. The effect of <u>type of annellation</u> on <u>conformation</u> and structure have been examined. In three cases the molecules are linked by <u>hydrogen bonds</u> in chains. In one structure four molecules are linked by hydrogen bonds to a water molecule. Comparison with anisotropic refinement shows that <u>isotropic refinement</u> using <u>low temperature data</u> gives equally good results at lower expense and with less work.			
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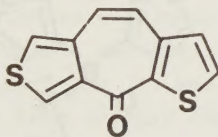
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1 INTRODUCTION

This review deals with a structural study of a set of cyclic organic compounds. These include two dithienotropones and several related substances. The present project was undertaken to investigate correlations between crystal structures and the chemical structure and properties, in particular the effects of annellation of heterocyclic rings on the tropone ring, the effect of changes in the type of annellation and the effect of substitution of carbon in the tropone ring by boron. The basic tricyclic fused ring system is similar to that of some well known psychotropic agents. A knowledge of the factors affecting the structures of these compounds can be of help for chemists and pharmacologists.

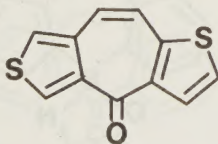
Details of studies on the individual compounds have been reported elsewhere as part of a larger investigation "X-Ray Crystallographic Studies on Cycloheptadithiophene Compounds and Similar Systems" carried out in the Department of Inorganic Chemistry 2, University of Lund.

I. The Crystal Structure of 9H-Cyclohepta[2,1-b:5,6-c']dithiophene-9-one¹



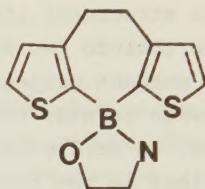
I

II. The Crystal Structure of 4H-Cyclohepta[1,2-b:4,5-c']dithiophene-4-one, $C_{11}H_6OS_2$ ²



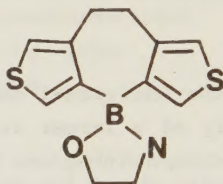
II

III. Spiro[9H-borepino(2,3-b:7,6-b')dithiophene-9,2'-(1,3,2)oxazaborolidine]³



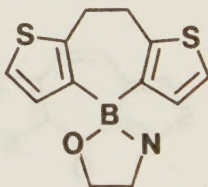
III

IV. The Crystal Structure of spiro[9H-borepino(2,3-c:7,6-c')dithiophene-9,2'-(1,3,2)oxazaborolidine], $C_{12}H_{14}BNOS_2$ ⁴



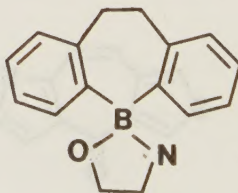
IV

V. The Crystal Structure of spiro[9H-borepino(1,2-b:5,6-b')dithiophene-9,2'-(1,3,2)oxazaborolidine]⁵



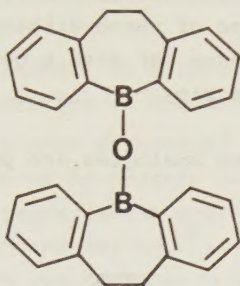
V

VI. The Crystal Structure of spiro[9H-borepino(b,f)dibenzo-9,2'-(1,3,2)oxazaborolidine]⁶



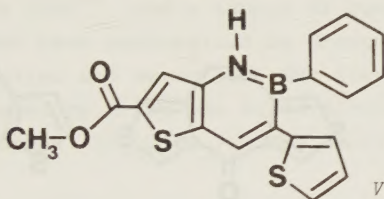
VI

VII. The Crystal Structure of bis(4-dibenzoborepinyl)ether, $(C_{14}H_{12}B)_2O$ ⁷



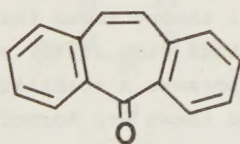
VII

VIII. The Crystal Structure of methyl 5-phenyl-6-(2-thienyl)-5,4-borazaro-benzo(b) thiophene-2-carboxylate⁸



VIII

The present work began with an examination of the simple tricyclic ketones I and II. Since the synthesis of 10,11-dihydro-5H-dibenzo-[a,d]cyclohepta-5-one (A) was reported in 1950-1951 a good deal of attention from organic chemists has been focused on the properties of this tricyclic ring system and its derivatives. The first X-ray structural study of a tricyclic system of this type with a 7-membered ring was made by Shimanouchi⁹.



(A)

A number of thiophene-annellated tropones and borepins have been prepared by Gronowitz and coworkers¹⁰⁻¹³. It was of interest here to investigate some of these dithiophene analogues of dibenzo-a,d-cycloheptanone (A) with a central non-benzenoid aromatic seven-membered ring.

Six isomeric dithiophene analogues are possible (Fig. 1):

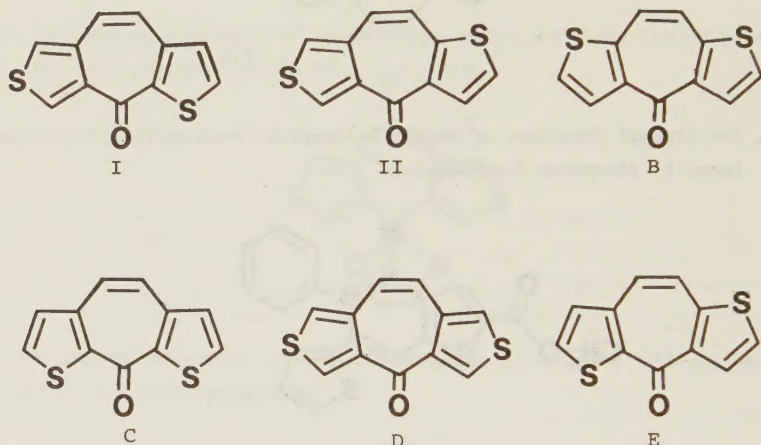


Fig. 1.

Compounds I and II have been investigated in this series, compound B has been examined by Andersson¹⁴; the remaining three presumably have similar crystal structures.

Many heteroaromatic systems have long been known. Most investigated are those with oxygen, nitrogen and sulphur. These are often rather similar, as explained by Hückels rule of aromaticity. Molecular orbital theory shows that benzene and other planar cyclic hydrocarbons with $(4n+2)$ π electrons (n being a non-negative integer) possess a stability not found in other unsaturated systems and these are termed aromatic. This concept has been generalised to fused carbocyclic systems and other heterocyclic systems. Thus hydrocarbons such as naphthalenes

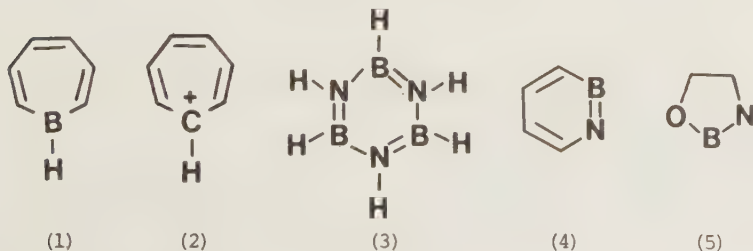
and phenanthrene and heterocycles such as thiophene, all of which have $4n+2$ π electrons, are aromatic.

Boron has been rather unusual as a heteroatom and the present boron compounds are therefore of special interest.

Organic boron compounds were discovered in the eighteensixties but a broad development of bororganic chemistry has come only during the last 20-30 years (see monographs and articles by Lipscomb¹⁵, Brown^{16,17} and Mikhailov¹⁸). Recent rapid progress in bororganic chemistry has been due to the considerable practical and theoretical importance of these compounds. As reagents boron compounds open up new synthetic methods for both organic and metallo-organic compounds.

A hetero seven-membered ring with boron was first synthesized by van Tamelen 1960¹⁹, and a number of compounds of this type have since then been synthesized by Gronowitz and coworkers¹³ during the sixties and seventies. The first compound of this type investigated by X-ray was bis(4-dithieno/3,2:2',3'-f/borepinyl)-ether, $(C_{10}H_6BS_2)_2O$, by Aurivillius²⁰.

Boron has three valence electrons, two of them in 2s orbitals and one in a 2p orbital. This allows three-coordination and also four-coordination with one bond of donor-acceptor character. Boron has one electron less than carbon and is therefore isoelectronic with C^+ ; borepin (1) is thus isoelectronic with tropylium ion (2). Some aromatic character might be expected.



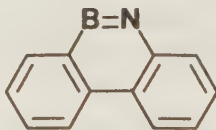
Spectroscopic evidence indicates that the borepin ring has aromatic character²¹.

The possibility of an N-B dative bond was first pointed out by Brown and Fletcher for triethanolamine borate (tritych boroxazolidine) in 1951²². The first substantial evidence for the existence of the N-B dative bond was obtained from the results of detailed kinetic studies by Zimmerman and coworkers²³ of the acid hydrolysis of these compounds.

When two neighbouring carbon atoms are replaced by boron and nitrogen atoms together (i.e. -B-N-) there is no net change in the numbers of valence electrons. Boron, carbon and nitrogen, with atomic numbers 5, 6 and 7, belong to the same period of the periodic table and a boron-nitrogen fragment has a similar orbital set available to that of a carbon-carbon fragment. Exchange of these two isoelectronic fragments should therefore give compounds with similar properties.

In six-ring systems we can compare borazine²⁴ (3) ("inorganic benzene") with benzene.

The boron-nitrogen fragment can be introduced into five- and six-membered aromatic systems such as borazarene (4), borazine (3) and oxazaborolidine (5). Hoffman^{25,26} has noted that the B-N fragment gives a higher stabilisation energy. Thus (6) is resistant to hydrolysis in conc. hydrochloric acid or strong sodium hydroxide; it can be nitrated, brominated and chlorinated.



(6)

In the present work five compounds with B-N bonds have been investigated.

The unexpected formation of a spiro ring on boron gave an opportunity for a study of this rather unusual grouping with tetrahedrally coordinated boron and nitrogen. These compounds also provide several examples of hydrogen bonding in different

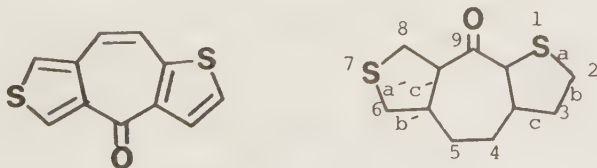
arrangements: N-H...O, O-H...O and O-H...N, and they show the effects of the thiophene ring annellation on the conformation and aromaticity of the central tropone or borepin rings of these molecules.

Several of the compounds investigated here have biological interest, at least indirectly. They have tricyclic ring systems similar to those of a number of psychotropic drugs. Over the last twenty years a number of analogous such as amitryptiline and imipramine have found use in medicine. The first of the boron-containing compounds examined here was supposed on chemical grounds to have an open chain attached to boron with some possibility of biological activity. However ring closure had occurred. Nonetheless this set of compounds has still some pharmacological interest since a knowledge of the factors affecting the structure and their relationship to biological activities can be important.

Nomenclature

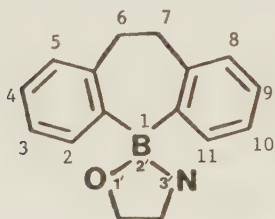
Different forms of nomenclature are used in the chemical literature for naming boron organic compounds. The most useful would be the IUPAC²⁷ rules but these are complex, especially for boron-containing heterocyclic compounds. Names for heterocyclic compounds with more than one heteroatom, according to IUPAC rules are given a prefix and number showing where the heteroatom is placed in the following order: O (oxa)... S (thia)... N (aza) ... B (bora). The compounds investigated here have five-membered rings and are thus named 1,3,2 oxazaborolidines.

Cycloheptadithiophenes

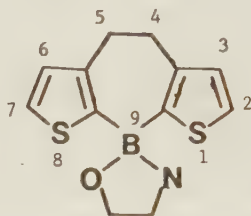


The base component is thiophene, since it is a hetero-ring. Its sides are specified by a,b,c (and a',b',c' for the second ring). These compounds are thus named as cycloheptadithiophen-ones. The entire system is numbered in a clockwise direction starting in the upper right corner.

Dibenzo- and dithieno-borepins with a spiro ring



VI

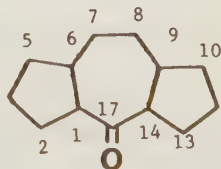
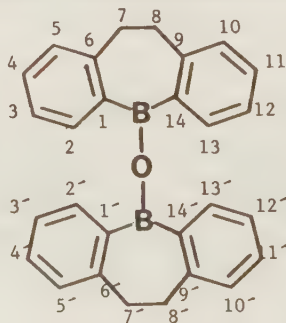
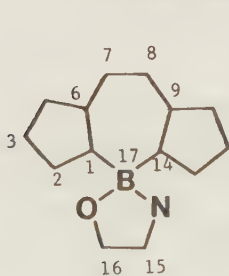


III

The base component is here borepin. Annellated benzene and thiophene rings are termed benzo or thieno. The "spiro"-prefix is placed before the names of the components with two numbers showing which atoms connect the rings. The numbering in the five-membered ring starts from oxygen so that the spiro-atom receives the lowest number. Thus compound III is:

Spiro-4,5-dihydro-9H-dithieno(2,3-b:7,6-b')borepin-9,2'(1',3',2')-oxazaborolidine

For simplicity the spiro compounds are drawn here with the spiro atom on the lower side and the numbering for the atoms does not follow chemical rules but is modified so that corresponding



bonds have the same numbering (see fig.above). The formal IUPAC names are inconveniently long and complicated and the main compounds here will be denoted by Roman numerals (see p.1 and table 1). Reference compounds of interest for comparison are denoted by Capital letters.

2 EXPERIMENTAL

Preparation and crystallization of the compounds

All compounds investigated were produced in the Department of Organic Chemistry, University of Lund, and were kindly provided for crystallographic investigation by prof S. Gronowitz. Substances I and II were synthesised and described by Yom-Tov¹¹, substances III-VII by Jeffries and Gronowitz¹³ and substance VIII by Ander²⁸.

Single crystals were obtained by recrystallization in several mixtures of organic solvents and at different temperatures using both water- and oilbaths and the crystallizing device described by Hope²⁹.

Spectroscopic data (UV, IR, NMR) for the compounds investigated have been given elsewhere¹⁰⁻¹³.

The densities of all compounds were measured by flotation.

Optical properties were checked with a polarisation microscope and showed good agreement with crystallographic properties.

Table 1 gives crystal and some physical data for the structures investigated and the identifying numbers used below in further discussion.

Unit cell dimensions and intensity data collection

Accurate cell dimensions were obtained from powder photographs taken at room temperature in a Guinier-Hägg camera with CuK_α radiation ($\lambda = 1.54056 \text{ \AA}$) and KCl ($a = 6.2928 \text{ \AA}$) as an internal standard.

θ -values of all measurable lines were used in the calculation of cell dimensions by least-squares. The minimizing function $\sum w(\sin^2 \theta_o - \sin^2 \theta_c)^2$ with $w = 1/\sin^2 2\theta$ was used.

Oscillation and Weissenberg photographs (zero and first layers) were taken for single crystals. Crystals chosen for measurements by the Weissenberg technique were as large as possible - to give sufficient intensity in a short time. Cell dimensions, Laue symmetry and space group were determined from the Weissenberg data.

Smaller crystals were chosen for data collection on the automatic diffractometer. All crystals were first checked with Weissenberg photographs and the cell parameters were then calculated using an accurate three-dimensional data set from the automatic diffractometer, taken at room temperature or low temperature depending on the data collection temperature used later. In each case, cell parameters from an accurate set of 50 reflexions were measured before and after data collection, using the same crystal and temperature adjustment.

Some crystal data are presented in Table 1. Three-dimensional data (see Table 2) were collected using several different instruments.

A Weissenberg integrating multifilm technique (Lund) was used for preliminary solution of structure VI. CuK_α radiation with Ni filter was used. The relative intensities were estimated using a microdensitometer for (0kl-7kl) reflexions. All other structures were determined from data obtained with the follow-

ing single crystal diffractometers.

A computer-controlled Enraf-Nonius CAD-4 (Lund, Rehovot Israel) at room temperature and at low temperature (liquid N₂ technique, ca 120 K).

A SYNTEX P21 (Davis USA, Moscow) both at room temperature and low temperature (liquid N₂ technique).

A Hilger (Moscow) single crystal diffractometer.

A Picker (Davis) automatic four-circle single crystal diffractometer with low temperature equipment (design by H. Hope) at ca 87 K with graphite monochromatized Cu or Mo radiation.

The X-ray intensities were measured with $\omega/2\theta$ or $\theta/2\theta$ scan techniques. Profile analyses were made in some cases to decide which scan mode was the most effective. The detector was a scintillation counter. Reflexions with intensities less than two (in some cases three) times the standard deviations were considered as unobserved. Three standard reflexions were measured during data collection at regular intervals (90-130 refl.) to check the stability of the crystals and orientation. Intensities which showed more than 5 % linear decay during the exposure were corrected. The intensity data were all corrected for Lorentz and polarisation effects. In some cases absorption corrections were made. Table 2 gives a summary of the data collection.

Determination and refinement of the structures

All structures were determined by direct methods using programmes GAASA³⁰, MULTAN-77³¹, Long's³² or Sheldrick's³³. All non-hydrogen atoms were found in this way. The localisation of hydrogen atoms in almost all cases was made from subsequent difference Fourier syntheses. Some hydrogen atoms were placed on calculated geometrical positions.

All structures were refined by the full-matrix least-squares method, cf Table 2.

The atomic scattering factors for non-hydrogen atoms were taken from Doyle and Turner³⁴ and for hydrogens from Stewart, Davidson and Simpson³⁵.

Calculations for I, II and IV were made on the UNIVAC 1108 at the University of Lund with computer programmes available in our department; the calculations for III, V and VI were performed on a CDC 7600 computer with programmes developed in the Department of Chemistry, University of California, Davis.

Calculations for compound VII were made on an ECLIPSE computer with the SYNTEX EXTL set of programmes at the Laboratory of Structural Chemistry, INEOS, Moscow. Calculations for VIII were made on the IBM 4341 in the WICC computing centre, with programmes from the Department of Structural Chemistry, Weizmann Institute of Science, Rehovot. All structures were refined isotropically. Some were also refined anisotropically. Correction for extinction was made for I and for anomalous scattering for III and V according to Hope³⁶. Values for f' and f'' were taken from Cromer and Liberman³⁷.

Some comments on the techniques used

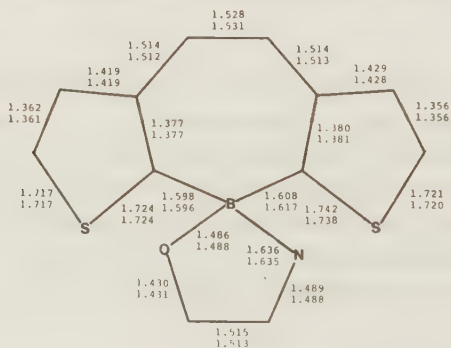
The use of several instruments and both Cu and Mo radiations for data collections made possible a comparison of different techniques.

Cell dimensions calculated from the powder data and from monocrystal data taken on a diffractometer are in good agreement. Both methods have different systematic errors. In the first case we have many small crystals with different orientation and in the second case there may be noncentric adjustment of crystals on the goniometer. It is thus desirable to check the cell dimensions with both methods.

Symmetry information from Weissenberg photographs is very important to ensure that the correct cell is chosen (symmetry elements can be seen here visually, while the diffractometer gives all mathematically possible cell dimensions). It is therefore advisable to make zero and first layer Weissenberg photographs.

During the solution of structures containing a spiro ring it was found that the thermal parameters were very large at room temperature for certain atoms (C15-C16). Thermal parameters (B_{ii} or U_{ii}) are approximately proportional in magnitude to the Kelvin temperature, so that lowering the temperature from 300 K to about 100 K will result in a reduction in B values roughly by a factor of three. With lower B values the isotropic temperature factor approximation very often becomes quite acceptable, giving B's for organic compounds around $1 \text{ \AA}^2$. Isotropic refinements with low temperature data from good crystals result in R values around 4-5 %. Because of the smaller amplitudes the resulting molecular geometry is much less affected by distortions associated with anisotropic motion. Structures III and VI were refined isotropically with good results. For structure V the low temperature was insufficient to freeze the equilibrium between the two conformers of the five-membered ring.

For comparison of isotropic and anisotropic refinements using low temperature data both were continued to completion for compound III. The figure below shows structure III with bond



lengths refined isotropically (upper value) and anisotropically (lower value). This gave $R_i = 4.2 \%$, $R_a = 2.9 \%$, $\sigma_{C-C} = 0.003 \text{ \AA}$. There is clearly no significant difference between isotropic and anisotropic bond lengths. (No difference is greater than 1σ).

Isotropic refinement using low-temperature data can be recommended because of the saving both in expense and in the work required³⁸.

Low temperature data collection eliminates difficulties with the adhesive (which becomes glass-hard) and there are no problems with drifting orientation matrix. Intensities are considerably increased (x50) especially at high 2θ values. The cold nitrogen atmosphere also gives protection from degradation due to reaction with oxygen or evaporation.

Table 1. Crystal data

Formula	Compound	Symmetry	Space group	Z	Unit cell dimensions (Å, °, Å ³)		
C ₁₁ H ₆ S ₂ O	I	monoclinic	P2 ₁ /c	4	a = 9.439(3)* b = 9.609(2) c = 11.198(3)	β = 112.92(2) V = 935	
C ₁₁ H ₆ S ₂ O ₂	II	orthorhombic	pbca	8	a = 7.847(2) b = 14.251(2) c = 16.922(1)	V = 1892	
C ₁₂ H ₁₄ S ₂ BNO	III	monoclinic	P2 ₁ /n	4	a = 8.625(1) b = 8.969(1) c = 16.892(2)	β = 103.03(1) V = 1273	
C ₁₂ H ₁₄ S ₂ BNO	IV	monoclinic	P2 ₁ /n	4	a = 9.684(1) b = 9.648(5) c = 13.437(1)	β = 96.97(1) V = 1246	
C ₁₂ H ₁₄ S ₂ BNO	V	orthorhombic	P2 ₁ ² ₁ ² ₁	8	a = 11.342(1) b = 11.804(1) c = 19.588(1)	V = 2622	
C ₁₄ H ₁₆ BNO	VI	monoclinic	P2 ₁ /n	4	a = 8.454(2) b = 9.171(2) c = 17.656(2)	β = 101.17(2) V = 1343	
C ₂₈ H ₂₄ B ₂ O	VII	orthorhombic	Pca2 ₁	4	a = 12.093(2) b = 13.223(2) c = 13.651(2)	V = 2183	
C ₁₈ H ₁₄ S ₂ BNO ₂	VIII	monoclinic	P2 ₁ /c	4	a = 16.222(1) b = 10.228(1) c = 10.369(1)	β = 106.46(1) V = 1650	

* Estimated standard deviations are given in parentheses in this and following tables.

Unit cell dimensions are calculated from data at different temperatures, depending on the temperature of later data collections.

Table 2. Data collection and refinement

Compound	I	II	III	IV	V	VI	VII	VIII
Apparatus	CAD-4	CAD-4	PICKER	CAD-4	SYNTEX P21	PICKER	HILGER	CAD-4
Temperature	295 K	295 K	87 K	295 K	150 K	87 K	295 K	80 K
Radiation	MoK α	CuK α	CuK α	CuK α	MoK α	MoK α	CuK α	MoK α
Wave length (Å)	0.71069	1.54056	1.5418	1.5418	0.7107	0.7107	1.5418	1.5418
k ($I_{\text{obs}} > k\sigma(I)$)	2.0	3.0	3.0	2.0	3.0	2.0	2.0	3.0
Scan technique	$\omega/2\theta$	$\omega/2\theta$	$\theta/2\theta$	$\omega/2\theta$	$\theta/2\theta$	$\theta/2\theta$	$\theta/2\theta$	$\theta/2\theta$
Max 2θ	55	55	130	60	55	55	54	54
Linear scaling	yes	yes	no	no	no	no	no	no
Intensity decrease %	11	6	-	7	3	-	7	-
Number of reflexions used in refinement	1168	1148	2130	2059	2671	2456	1377	2810
Number of reflexions measured	2291	1787	2130	2354	3057	2890	1984	3597
Average $\sigma_{\text{C-C}}$ (Å)	.005	.005	.003	.005	.004	.003	.02	.003
Thermal parameters	aniso	aniso	aniso	aniso	iso	iso	aniso	aniso
R	.041	.042	.030	.049	.059	.049	.073	.057
R_w	.056	.048	.029	.060	.068	.063	.077	.059
μ (cm ⁻¹)	5.1	28.4	35.6	35.6	6.2	0.6	5.0	2.8

3 DESCRIPTION OF THE CRYSTAL STRUCTURES AND DISCUSSION

The compounds investigated in this project can be divided into three main groups: (1) those with a carbocyclic seven-membered ring, the dithienotropones, (2) those containing three-coordinated boron and (3) those with a seven-membered ring containing four-coordinated boron.

3.1 Dithienotropones

Of the six possible dithienotropones (see Fig. 1), three have been investigated crystallographically (see p. 4). Bond lengths, angles and degree of aromaticity are given for the thiophene rings in Table 3 and for tropone rings in Table 4. Stereoscopic views of projections in the best plane of the molecule and in a plane perpendicular to it are shown in Figs. 2 and 3 for compounds I and II. The packing is shown in Fig. 12 and 13.

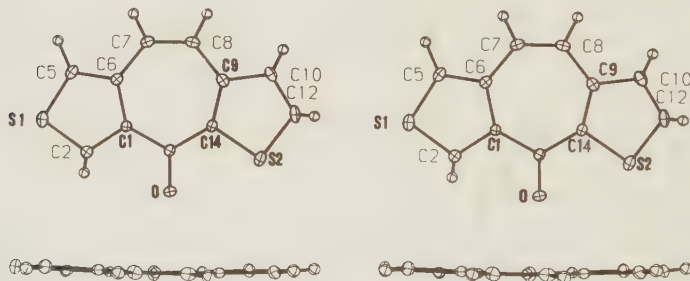


Fig. 2. Compound I

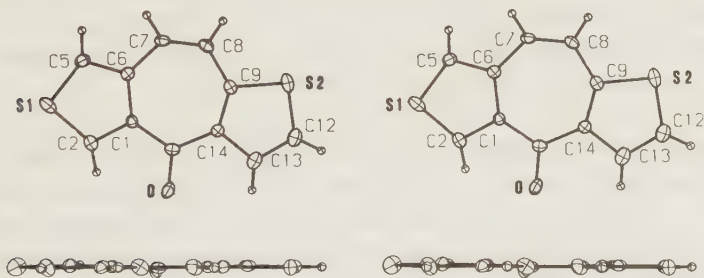
Both compounds in this group are ketones with a central seven-membered ring with ethylene bridge ($C7=C8$) and two thiophene side rings with different types of ring annellation.

Crystallographic data is also available for several other compounds of similar type. Of these compounds B^{14} , F^{20} and G^{39} have thiophene side rings with b,b annellation; the remainder all have benzo side rings (see Table 4). Compound F^{20} has $C17$ replaced

by three-coordinated boron and in compound N⁴⁰ there is three-coordinated nitrogen.

Bond lengths. In the thiophene rings bond lengths are, in general, in good accord with thiophene itself. The C-C bonds in both compounds, independently of type of annellation, are 1.427-1.437(6) Å, while thiophene has 1.423(2) Å. The free C-S bond lengths are 1.672-1.684(5) Å, significantly shorter than the linked C-S bond of 1.723(3) Å; thiophene itself has 1.714(2) Å.

The C=C bond lengths are dependent on the type of annellation to the seven-membered ring. If the thiophene double bond is coincident with a double bond in the seven-membered ring system it has double bond character. Thus in compounds I and II these double bonds are 1.373-1.387 Å and in compound B,¹⁴ F²⁰ and G³⁹ 1.389-1.396 Å. The free C12=C13 bond of 1.348(7) Å in compound II is rather short, which can be a consequence of the conjugated system S-C=C-C=O. The C1=C2 bond length in compound I of 1.425 Å



has double bond character, 1.373-1.387 Å, slightly longer than in tropone itself; with c-annellation the bond length is significantly longer, 1.433-1.437(5) Å. Other bond lengths in the tropone ring are consistent with those of tropone. On replacement of the carbonyl group by boron in compound F the corresponding bonds (C1-C17, C14-C17) are much longer (1.533 Å). When replaced by nitrogen (with the same three-coordination) these bonds are rather shorter (1.409 Å) see Table 4. If the side rings are benzenes the annellating bonds have benzene bond lengths. The C=O carbonyl bond is slightly longer (1.228, 1.295 Å) than the usual value (1.215 Å, Sutton, 1965)⁴¹.

Angles. In the thiophene rings the angles are similar to those in thiophene but there are small variations due to the annellation type. In a flat seven-membered ring angles in the ring are 128.5°. In tropone⁴² the ring has a boat form. The angles at C6 and C9 are 128° as in a flat ring while the angle at the carbonyl group is 113.8° and remaining angles are around 120°. In the present compounds the angle at carbonyl is 120° and 122°, the other angles are very close to 128.5°, except for the angles closest to the sulphur atom in the b-annellated compounds, which are significantly larger (132.9-133.3°).

Planarity. The thiophene rings are all quite planar (see torsion angles in Table 7). The central tropone ring may have either boat, chair or plane conformations. The optimum conformation for cycloheptatrienes has been discussed by Butcher⁴³, Traetteberg⁴⁴ and Dashewsky⁴⁵. According to them the most stable conformation should be "boat" but Dashewsky has shown that the energy difference between boat and plane conformations should be small.

In the present compounds the central seven-membered ring is planar (see torsion angles in Table 7). The percentage deviations from expected values of the angles in the tropone ring for the dithienotropones are less than for the corresponding angles in the dibenzo compounds.

All the thieno tropones are nearly planar (see table 7). However when the tropone ring has annellated benzo rings (A,⁹ K,⁴⁷ L⁴⁸) it has angular strain. The sum of the internal angles for

the dibenzotropones ($850-870^{\circ}$) is much less than the theoretical value for a flat ring (899.9°). The tropone ring and thus the tricyclic ring system is bent. In all three dithienoannellated tropones the sum of the angles in the tropone is close to the theoretical value (I: 899.7° , II: 899.9° , B: 899.3°). In all three cases the tropone ring and the tricyclic ring system are planar.

It is of interest here that the thiophene rings apparently flatten out the tricyclic ring system; in the dibenzo analogues (A, K, L, M⁴⁹) the side rings are set at a marked angle (see Table 4).

Table 3. Bond lengths, angles and aromaticity in thiophenes

Bond lengths

Compound	C=C		C-C		C-S
	annel				linked
I	1.373 (7) ^o 1.380 (5)	1.387 (5) ^o 1.424 (5)	1.427 (6) 1.433 (5)	1.680 (5) ^o 1.681 (4) 1.672 (3)	1.723 (3)
II	1.348 (7)	1.373 (5) 1.378 (6) 1.368 (5)	1.435 (6) 1.437 (5)	1.684 (5) 1.674 (5) 1.675 (5)	1.723 (3)
III	1.360 (3) 1.356 (3)	1.377 (3) 1.381 (3)	1.419 (3) 1.428 (3)	1.717 (2) 1.720 (2)	1.724 (2) 1.738 (2)
IV	1.360 (5) 1.355 (4)	1.390 (5) 1.373 (4)	1.439 (4) 1.440 (4)	1.712 (3) 1.716 (3) 1.688 (3) 1.701 (3)	
Va	1.394 (3) 1.384 (3)	1.395 (3) 1.394 (3)	1.456 (3) 1.441 (3)	1.722 (3) 1.726 (3)	1.754 (2) 1.758 (2)
Vb	1.395 (3) 1.374 (3)	1.391 (3) 1.392 (3)	1.450 (3) 1.462 (3)	1.725 (3) 1.724 (3)	1.748 (3) 1.756 (3)
VIII	1.347 (3) 1.368 (4)	1.399 (4) 1.392 (3)	1.430 (3) 1.416 (3)	1.707 (4) 1.731 (4)	1.731 (3) 1.735 (3)
B ¹⁴	1.348 (5) 1.341 (5)	1.389 (5) 1.396 (5)	1.424 (5) 1.427 (5)	1.711 (4) 1.721 (4)	1.738 (4) 1.737 (4)
G ³⁹	1.373 (13) 1.345 (15)	1.432 (12) 1.391 (14)	1.441 (13) 1.440 (12)	1.730 (10) 1.692 (11)	1.742 (9) 1.726 (9)
F ²⁰	1.346 1.343	1.384 1.390	1.423 1.425	1.694 1.692	1.724 1.727
H ⁴⁶ thiophene	1.370 (2)		1.423 (2)	1.714 (2)	

Angles

Compound	C-S-C		C=C-S		C=C-C		Aromaticity	
			ann	fri	ann		A	
I	92.8 (2) ^o 93.6 (2)	111.3 (3) ^o 113.2 (3)	111.6 (3) ^o 110.9 (3)	113.6 (4) ^o 110.6 (3)	110.7 (3) ^o 111.6 (3)		.94	.94
II	92.7 (3) 92.3 (3)	112.4 (4) 113.3 (3)	110.5 (4) 112.6 (3)	112.6 (4) 110.6 (4)	111.9 (3) 111.1 (4)		.89	.84
III	93.2 (1) 93.2 (1)	110.8 (1) 110.6 (1)	109.6 (1) 109.6 (1)	112.9 (2) 113.9 (2)	113.5 (2) 112.8 (2)		.93	.90
IV	91.2 (2) 91.9 (2)	112.6 (3) 113.2 (2)	111.4 (3) 113.6 (3)	110.8 (3) 111.5 (3)	113.4 (3) 110.3 (3)		.87	.91
Va	92.6 (2) 92.3 (2)	111.0 (2) 110.9 (3)	111.9 (2) 111.5 (3)	114.0 (2) 114.4 (3)	110.6 (3) 110.9 (3)		.91	.93
Vb	92.6 (2) 92.5 (2)	110.9 (3) 110.6 (3)	111.8 (3) 111.9 (3)	114.6 (3) 113.9 (3)	110.1 (3) 110.8 (3)		.92	.84
VIII	92.6 (2) 91.0 (2)	112.2 (2) 110.0 (2)		113.3 (2) 111.9 (2)				
		112.8 (2)	111.3 (2)	111.9 (2)	113.0 (2)			
B ¹⁴	92.1 (3) 92.3 (2)	111.8 (4) 111.6 (4)	110.4 (3) 110.2 (3)	113.9 (4) 114.2 (4)	111.7 (4) 111.6 (4)		.89	.85
G ³⁹	91.8 (7) 90.7 (5)	113.4 (10) 115.0 (8)	110.7 (9) 111.8 (6)	112.4 (10) 111.3 (9)	111.6 (9) 111.2 (8)			
F ²⁰	92.1 92.0	112.1 111.9	111.2 111.5	114.3 111.4	110.3 110.4			
H ⁴⁶ thiophene	92.2 (1)	111.5 (2)		112.5 (2)			.93	

Table 4. Tropones; bond lengths, angles and aromaticity

Distances (Å)



Compound	1-6	6-7	7-8	8-9	9-14	14-17	17-1	17-0
I	1.433 (5)	1.442 (5)	1.341 (6)	1.445 (5)	1.387 (5)	1.474 (4)	1.453 (5)	1.228 (4)
II	1.437 (5)	1.447 (5)	1.332 (5)	1.431 (6)	1.373 (5)	1.480 (5)	1.469 (5)	1.295 (5)
B	1.396 (5)	1.421 (5)	1.353 (5)	1.428 (5)	1.389 (5)	1.469 (5)	1.465 (5)	1.240 (5)
A	1.406	1.462	1.352	1.462	1.406	1.465	1.465	1.260
F	1.390	1.427	1.332	1.426	1.384	1.533	1.533	
Troponone ⁴²	1.355	1.452	1.357	1.452	1.355	1.463	1.463	
J ⁴⁴	1.356 (5)	1.446 (7)	1.356 (5)	1.446 (7)	1.356 (5)	1.505 (7)	1.505 (7)	
K ⁴⁷	1.418 (2)	1.461	1.330	1.454	1.418	1.490	1.491	
L ⁴⁸	1.414 (3)	1.460 (4)	1.325 (5)	1.452 (4)	1.402 (3)	1.488 (3)	1.488 (3)	
M ⁴⁹	1.427	1.464	1.328	1.431	1.398	1.492	1.479	
N ⁴⁰	1.402 (2)	1.465 (2)	1.322 (2)	1.465 (2)	1.402 (2)	1.409 (2)	1.409 (2)	

Angles (°)

Compound	17	1	6	7	8	9	14	Aromaticity
I	120.6 (3)	130.8 (3)	128.8 (3)	128.6 (4)	129.0 (4)	128.5 (3)	133.4 (3)	.82
II	122.4 (3)	130.5 (3)	128.4 (4)	129.4 (4)	127.2 (7)	133.3 (4)	128.7 (3)	.80
B	122.5 (4)	128.7 (4)	132.9 (4)	127.1 (4)	126.4 (4)	133.2 (4)	128.5 (4)	
F	124.1	126.2	132.5	128.7	129.5	131.7	127.1	
J ⁴⁴	113.0	121.8	127.2	119.8	119.8	127.2	121.8	
K ⁴⁷	114.9	120.4	124.1	127.8	127.7	123.5	121.6	
L ⁴⁸	114.9 (2)	120.3 (2)	124.4 (2)	127.8 (3)	128.0 (2)	123.4 (2)	121.4 (2)	
M ⁴⁹	120.1	120.9	124.0	130.4	128.8	124.6	122.5	
N ⁴⁰	123.4 (1)	121.4 (1)	123.1 (1)	129.2 (2)	129.2 (2)	123.1 (1)	121.4 (1)	.69

3.2 Compounds with three-coordinated boron

To examine the effect of replacement of a carbon atom by a boron atom in the seven-membered ring the structure of F, the analogue of the dithienotropones, was determined by Aurivillius. The next step was to replace the ethylene bridge ($-\text{CH}=\text{CH}-$) by the dimethylene bridge ($-\text{CH}_2-\text{CH}_2-$) in compound VII. Compound F with the ethylene bridge is still planar and aromatic (Table 4). In compound VII with a dimethylene bridge (Table 5 and Fig. 4) the two side rings are set at a marked angle as in the case of the dibenzocycloheptane analogue (imipramine)⁵³. Boron, the attached carbons and the oxygen lie in a plane. The benzene rings are planar and the carbons, C7/C8, lie in the same plane as the ring

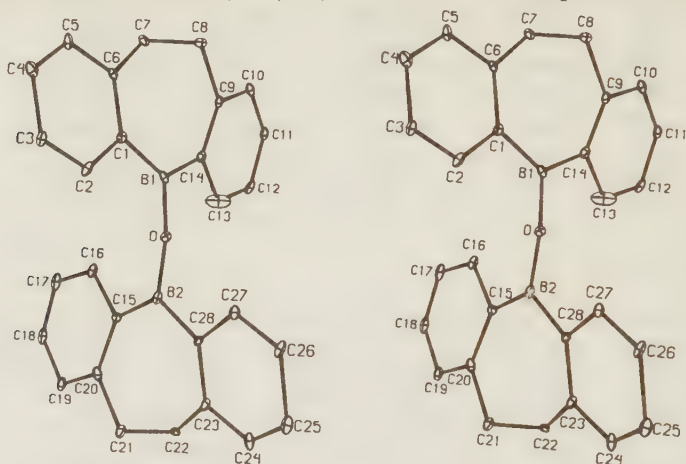


Fig. 4. Compound VII

to which they are attached. The B-O-B bonds joining the two tricyclic ring systems form an angle ($^{\circ}$) and the ring systems are set almost at a right angle.

Bond lengths. The data for compound VII have relatively large standard deviations. (Inferior crystals; Hilger diffractometer). The B-C distances (average 1.565 Å; for compound F - 1.533 Å) are shorter than for tetrahedrally coordinated boron (average 1.610 Å) in compounds III-VI.

The values for compound VIII, which are more accurate, are

1.550 and 1.582 Å. The O-B distance here (average 1.340 Å) is slightly shorter than the O-B distance for four-coordinated boron in the oxazaborolidine ring of compounds III-VI (average 1.488 Å). The C6-C7, C7-C8, C8-C9 bonds are standard single bonds.

Angles. The angle C-B-C in the seven-membered rings (about 127°) is significantly larger than expected. In the dithienotropones I and II it is 120.6 and 122.4° , in compound F it is 124.1° . The sum of the angles in the seven-membered ring is 849° indicating that there is a large "angle strain". The seven-membered ring in accordance is not planar.

Compound VIII has three-coordinated boron (Fig. 5) but no seven-membered ring. The fused dicyclic ring system is planar. The attached thiophene ring and the methoxycarbonyl group lie in the same plane; the phenyl ring lies at right angle to this plane.

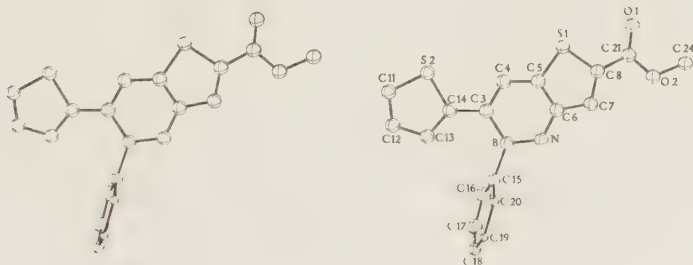
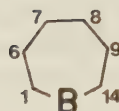


Fig. 5. Compound VIII

Bond lengths. The B-N length of 1.414 Å is shorter than the length of the "aromatic" B-N bonds in $N_3B_3H_6$, in $N_3B_3(C_6H_5)_6$ (Lux et al.^{24,50}; 1.423-1.447 Å) and found in hexachloroborazine⁵¹ (1.423(1) Å). The C-S bonds in the two thiophene rings are rather long (1.731(3) Å).

Table 5. Borepin and related seven-membered hetero rings
Bond lengths (Å)



	C1-C6	C6-C7	C7-C8	C8-C9	C9-C14	C14-B17	B17-C1	
Compound								
III	1.377(3)	1.512(3)	1.531(3)	1.513(3)	1.381(3)	1.611(3)	1.596(3)	
IV	1.439(4)	1.501(4)	1.540(5)	1.504(5)	1.440(4)	1.616(3)	1.599(3)	
Va	1.395(4)	1.509(4)	1.548(5)	1.507(4)	1.394(3)	1.606(2)	1.612(3)	
Vb	1.391(4)	1.522(4)	1.543(4)	1.517(4)	1.392(2)	1.606(3)	1.630(3)	
VI	1.410(2)	1.512(2)	1.541(3)	1.527(3)	1.410(3)	1.622(3)	1.608(3)	
VII	1.404(17)	1.510(18)	1.580(19)	1.505(18)	1.364(17)	1.584(19)	1.564(19)	
	1.411(17)	1.483(22)	1.541(20)	1.573(23)	1.420(17)	1.563(24)	1.543(24)	
O ⁵²	1.389(5)	1.535(5)	1.523(5)	1.500(5)	1.400(5)	1.504(5)	1.520(5)	
P ⁵³	1.392(5)	1.508(9)	1.508(7)	1.503(4)	1.418(7)	1.426(6)	1.423(5)	
	1.396(6)	1.521(7)	1.408(8)	1.474(9)	1.407(7)	1.421(5)	1.433(4)	
Q ⁵⁴	1.402(7)	1.511(7)	1.509(5)	1.504(8)	1.405(7)	1.393(5)	1.406(5)	
	1.406(5)	1.507(5)	1.519(7)	1.499(4)	1.391(3)	1.399(4)	1.393(4)	
R ⁵⁵		1.520(14)	1.518(15)	1.498(11)	1.418(10)	1.551(9)	1.563(9)	
Angles (°)								
	17	1	6	7	8	9	14	α
Compound								
III	111.0(2)	127.3(2)	121.5(2)	113.0(2)	116.8(2)	127.8(2)	132.5(2)	131.7°
IV	115.5(2)	124.7(2)	122.1(3)	112.0(3)	115.9(3)	126.9(3)	129.6(3)	140.4
Va	120.0(2)	126.2(2)	129.8(2)	114.5(2)	113.9(2)	131.2(2)	128.1(2)	
Vb	116.1(2)	123.4(2)	127.2(2)	111.8(2)	114.5(2)	132.2(2)	129.1(2)	
VI	118.0(2)	122.0(2)	120.1(2)	112.7(2)	118.8(2)	125.0(2)	126.5(2)	138.0
VII	127.9(10)	124.5(11)	125.3(11)	113.6(11)	110.8(10)	120.2(11)	127.4(11)	
	126.6(15)	129.4(14)	118.4(11)	112.7(13)	110.9(12)	123.4(12)	124.9(13)	
O ⁵²	114.6(2)	124.6(2)	125.2(2)	120.3(2)	113.3(2)	119.4(2)	119.4(2)	123.1
P ⁵³	120.8(3)	120.3(4)	118.4(4)	110.2(4)	117.1(4)	126.7(4)	123.8(3)	130.3
	115.8(4)	118.6(3)	118.4(3)	115.0(6)	121.6(5)	126.4(5)	120.8(4)	123.1
Q ⁵⁴	131.9(4)	124.9(4)	125.0(4)	114.6(3)	111.6(5)	120.5(3)	122.0(3)	151.3
	132.7(3)	125.7(3)	125.0(3)	114.8(4)	112.8(2)	121.1(3)	123.1(3)	154.1

3.3 Tetracyclic compounds with four-coordinated boron

Four related substances with a fused tricyclic system and a spiro-oxazaborolidine ring have been investigated. In all cases the spiro boron atom connects the two side rings and is approximately tetrahedrally coordinated. (The smallest angle is 99.1° and the largest 120° , see Table 6). The spiro ring lies roughly at a right angle to the fused ring system.

Distances, angles and torsion angles are given in Tables 5-7. Stereoscopic views of these structures are shown in Figs. 6-10. The packing is shown in Figs. 13-16. Tetrahedrally coordinated boron in tetraphenyl borate gives B-C bond lengths of 1.64 Å. The B-C bond lengths measured here are significantly shorter (average 1.610 Å). The three-coordinated boron compounds discussed earlier have much shorter average B-C bond lengths (1.565 Å).

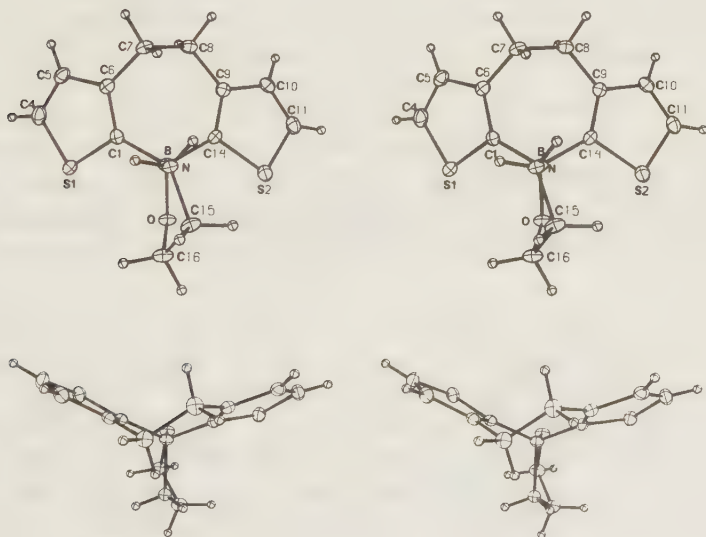


Fig. 6. Compound III

The fused tricyclic ring system

Three of these compounds have thiophene rings with different types of annellation, the fourth is the dibenzo compound. In compounds III, IV, VI and conformer Vb the two side rings are set at a marked angle. Thiophene and benzene rings here are planar and the attached carbon (C7/C8) lies in the same plane. Boron lies at the intersection of these two planes. The dihedral angle α between the side rings ranges from 131° to 140° (see Table 5) except for conformer Va which is nearly planar ($^\circ$).

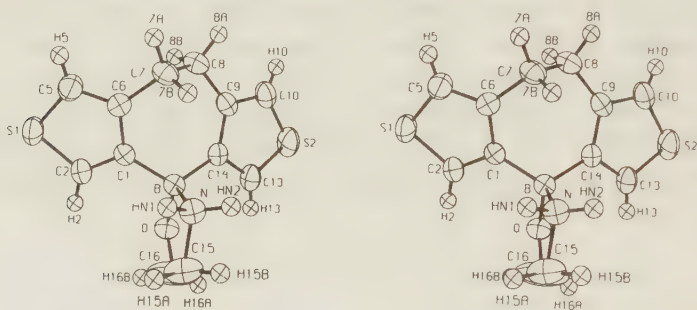


Fig. 7. Compound IV

The seven-membered ring has two possible conformations depending on whether the dimethylene bridge is twisted to the left or to the right. Both conformations are present in the crystal in compounds III, IV and VI. In compound V there are two independent molecules with different conformations of the tricyclic ring

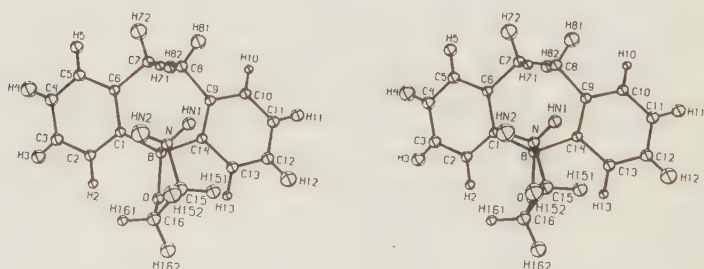


Fig. 8. Compound VI

system but only one conformation of the dimethylene bridge in each crystal.

Bond lengths. The variations in the annellation of the side rings and in the placing of the heteroatoms interact with each other giving very complicated effects on bond lengths and angles. As for the dithienotropones the C-S bonds linked to the central ring are longer than in thiophene (1.724-1.758 Å). The C1-C6 and C9-C14 bond lengths are in general in accord with the bond lengths specified by the side rings. Thus, bonds with c-annellated thiophenes are much longer (1.439 Å) than others (1.383, 1.351, 1.377 Å). The C7-C8 bond is a normal single bond (1.531-1.538 Å) while the C6-C7 and C8-C9 bonds connected to the aromatic side rings are slightly shorter than normal single bonds (1.501-1.527(4) Å).

Angles. The angles at C1 and C6 are 3° smaller than angles at C9 and C14. At C7 and C8 the angles are 111.8-118.8 $^\circ$. This is much larger than the tetrahedral angle of 109.5 $^\circ$. The angles in the thiophene and benzene rings have normal values. The sum of the angles of the seven-membered rings varies around 843-863 $^\circ$ and is significantly less than the sum of the angles in a flat ring.

In molecules III and VI the seven-membered ring can be described as a somewhat twisted boat. In molecules IV, Va and Vb the seven-membered ring has a twist conformation (see Table 7).

Half normal probability plots^{60a} show that it is not possible to derive mean values of the two halves of the molecules III-VI. The two sides of the molecule are not identical. There are significant differences in distances and angles and the annellated thieno and benzo rings make different angles with the central ring. These molecules have therefore only pseudo-mirror symmetry. The lack of symmetry of the molecule is due to the dimethylene bridge, one side of which is "up" and the other "down".

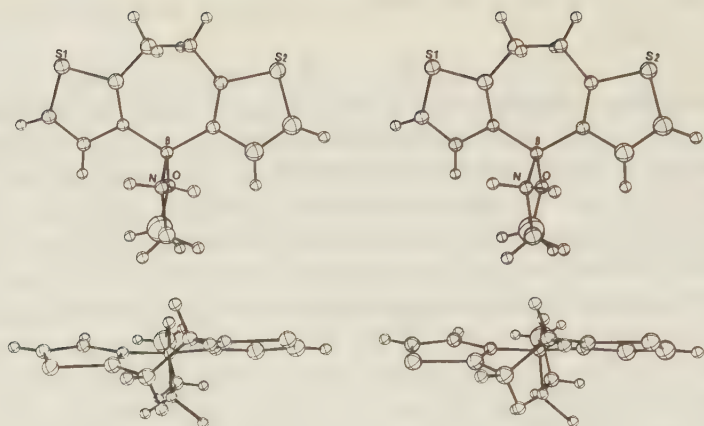


Fig. 9. Compound Va

Three of the substances with oxazaborolidine rings described by Rettig & Trotter⁵⁶⁻⁵⁹ are of interest since they have two benzene rings or equivalent groups attached to boron. In these there is no constraining dimethylene bridge. The aromatic rings in these compounds lie at a much greater angle (about 74°) than the aromatic rings of the compounds described here.

Table 6. Oxazaborolidines and arrangement around boron
Bond lengths (Å)



Compound	O-B	B-N	C15-N	C15-C16	C16-O	B-Cl	B-Cl4
III	1.488 (2)	1.635 (3)	1.488 (2)	1.513 (3)	1.431 (2)	1.596 (3)	1.611 (3)
IV	1.477 (4)	1.653 (3)	1.460 (5)	1.442 (7)	1.379 (6)	1.599 (3)	1.616 (3)
Va	1.527 (3)	1.686 (3)	1.504 (4)	1.476 (6)	1.429 (3)	1.612 (3)	1.606 (3)
Vb	1.498 (3)	1.695 (3)	1.502 (4)	1.532 (6)	1.420 (3)	1.630 (3)	1.606 (3)
V1	1.492 (3)	1.658 (3)	1.492 (3)	1.519 (3)	1.425 (3)	1.608 (3)	1.622 (3)
S ⁵⁶	1.484 (3)	1.653 (3)	1.485 (3)	1.505 (4)	1.413 (3)	1.611 (2)	1.611 (2)
T ⁵⁷	1.476 (2)	1.655 (2)	1.489 (2)	1.507 (3)	1.409 (2)	1.613 (2)	1.620 (2)
U ⁵⁸	1.471 (4)	1.652 (4)	1.491 (4)	1.494 (4)	1.418 (4)	1.616 (4)	1.620 (4)
V ⁵⁹	1.478 (3)	1.657 (3)	1.488 (3)	1.501 (4)	1.413 (3)	1.613 (3)	1.619 (3)

Angles (°)

Compound	O-B-N	B-N-C15	N-C15-C16	C15-C16-O	C16-O-B	O-B-Cl	O-B-Cl4	N-B-Cl	N-B-Cl4	Cl-B-Cl4
III	100.4 (1)	105.0 (1)	102.2 (2)	104. (2)	111.6 (1)	114.1 (2)	111.5 (2)	109.9 (2)	109.4 (2)	111.0 (2)
IV	100.2 (2)	105.6 (2)	108.6 (4)	110.4 (4)	113.9 (3)	112.3 (2)	111.2 (2)	108.2 (2)	108.2 (2)	115.5 (2)
Va	99.1 (2)	106.5 (3)	107.3 (3)	108.7 (4)	113.5 (3)	110.3 (2)	110.4 (2)	107.4 (2)	107.5 (2)	120.0 (2)
Vb	99.1 (2)	105.6 (2)	102.6 (2)	104.8 (2)	111.0 (2)	114.4 (2)	111.6 (2)	109.7 (2)	107.5 (2)	116.1 (2)
V1	99.8 (2)	104.9 (2)	102.2 (2)	104.8 (2)	112.0 (2)	111.5 (1)	111.0 (2)	109.0 (2)	105.7 (1)	118.0 (2)
S ⁵⁶	99.7 (1)	106.1 (2)	102.9 (2)	105.2 (2)	110.1 (2)	108.9 (2)	113.7 (2)	112.9 (2)	106.8 (2)	114.0 (2)
T ⁵⁷	98.4 (1)	105.5 (1)	105.2 (1)	106.0 (1)	107.7 (1)	112.1 (1)	112.2 (1)	109.8 (1)	109.6 (1)	113.6 (1)
U ⁵⁸	99.9 (2)	105.5 (2)	105.0 (2)	106.0 (2)	108.2 (2)	110.4 (2)	112.9 (2)	110.7 (2)	107.7 (2)	114.2 (2)
V ⁵⁹	99.9 (1)	105.3 (2)	104.4 (2)	105.3 (2)	107.8 (2)	110.1 (2)	113.4 (2)	111.0 (2)	107.3 (2)	114.2 (2)

Compounds III-VII have a five-membered oxazaborolidine spiro ring. This lies approximately at a right angle to the best plane of the fused tricyclic ring system. The B-N bond is usually quasi-axial to the seven-membered ring; presumably ring closure occurs most easily from this face of the molecule.

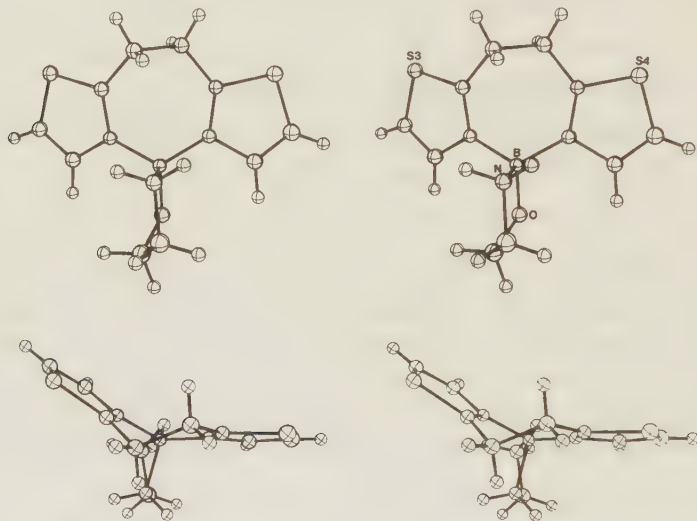


Fig. 10. Compound Vb

Bond lengths. The bond lengths are in reasonable agreement in all the structures investigated (Table 6) except for structure IV and Va (see Experimental) which show significant deviations. The major discrepancy is in the C15-C16 distance of 1.442(2) Å in IV and 1.476 Å in Va. This is due to the presence of two rapidly interchanging twist conformers. This appears as large B values for atom C16 as shown by the thermal ellipsoids (see Figs. 7 and 9). The apparent bond distance is measured between two average positions and is therefore significantly shortened. This effect may also appear elsewhere, for instance in the short C16-O bond length of 1.379(2) Å in compound IV. Long distance effects of annellation type might also contribute here.

Angles. The angles in all compounds are in reasonable agreement, again with the exception of IV and Va. The OBN angle is constant. The sum of the interior angles is much smaller than for a flat five-membered ring but the angles at C15, C16 and O are markedly larger in IV and Va than in the remaining compounds. This appears to be the result of the interconverting conformers. The resultant deviations from planarity and the corresponding torsion angles are shown in Table 7.

There are two possible types of conformation: twist and envelope. The selection of which atoms are twisted out of the OBN plane will depend on crystal packing effects and on the hydrogen bonds. Calculations by Hendrickson^{60b} indicate that there are four conformations of minimum energy. In four of the compounds (III, Va, Vb, VI) this ring has a twist conformation. In IV the conformation is apparently envelope but this can be regarded as a hybrid of two twist conformers in dynamic equilibrium.

A set of compounds with oxazaborolidine rings has been described by Rettig & Trotter⁵⁶⁻⁵⁹ (see Table 6). Bond lengths and angles in these compounds and in those described here are consistent. The oxazaborolidine ring in the Rettig & Trotter compounds shows corresponding variations in conformation.

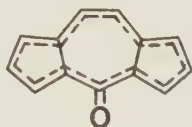
Table 7. Torsion angles ($^{\circ}$)

Atoms	III	IV	Va	Vb	VI	VII
B-C1-C6-C7	1.3	7.5	8.5	- 2.6	6.4	0
C1-C6-C7-C8	47.5	64.7	47.5	27.2	65.9	49.3
C5-C6-C7-C8	-108.8	-111.5	-131.8	-155.5	-111.9	-135.5
C6-C7-C8-C9	- 69.0	- 78.7	- 72.5	- 70.2	- 78.1	- 88.0
C7-C8-C9-C10	-164.6	-150.9	-135.5	-111.6	-153.4	-123.6
C7-C8-C9-C14	18.5	31.5	41.4	67.4	28.9	55.0
C8-C9-C10-C11	-178.9	- 19.2	-177.5	-179.8	178.6	-179.2
C8-C9-C14-C13	178.6	178.0	-178.0	179.8	178.4	178.8
C8-C9-C14-B	1.0	- 2.6	2.7	- 2.4	- 6.4	- 5.9
C9-C14-B-C1	28.9	24.8	- 3	- 40.9	35.6	28.0
C9-C14-B-N	- 92.6	- 96.6	-125.9	- 82.4	- 86.6	-
C9-C14-B-O	157.3	154.1	127.1	-170.0	166.1	157.0
C14-B-C1-C6	- 48.3	- 48.4	- 23.8	24.3	- 56.1	0.3
C14-B-N-C15	- 99.9	124.5	-108.8	121.1	- 99.0	-
C14-B-O-C16	123.9	115.0	120.7	- 91.5	120.8	-
C1-B-N-C15	138.0	109.3	120.8	-111.8	133.3	-
C1-B-O-C16	-109.4	-114.1	-104.4	136.9	-105.4	-
B-N-C15-C16	- 34.8	13.1	- 17.4	- 26.6	- 34.2	-
N-C15-C16-O	40.4	- 13.3	23.1	40.8	40.9	-
C15-C16-O-B	- 30.5	7.5	- 19.9	- 40.3	- 31.8	-
C16-O-B-N	8.1	2.8	8.1	21.5	9.1	-
O-B-N-C15	17.5	- 8.5	6.0	4.9	16.3	-

3.4 Aromaticity

The fused three-ring systems make possible an extended conjugated double bond system which in these compounds can be stabilised by π -electron delocalisation.

The resonance structure can be shown schematically as follows:



implying conjugation and aromatic properties. Planar molecules e g I, II and B allow a large overlap between π -orbitals. The heteroatoms are not only electron donors affecting the formation of an aromatic π -electron system, they also direct electrophilic and nucleophilic attack. In fused ring systems the physical properties and reactivity are strongly affected by the nature of the condensed rings and the relative positions of heteroatoms^{61,62}, i.e by the type of annellation.

Of the present compounds I and II are planar and appear to be extended aromatic systems. Bond lengths in Table 3 and 4 show that single bonds are markedly shortened (1.421-1.480 Å), indicating electron delocalisation in accordance with aromatic systems.

The aromatic properties of cycloheptadithiophenes have been studied by Yom-Tov⁶³ by chemical and spectroscopic methods. These suggest a highly polarised carbonyl bond.

As a measure of aromaticity Julg⁶⁴ suggested the equation $A = 1 - k \sum (l_i - \bar{l})^2 / n \bar{l}^2$, where A is the degree of aromaticity, n is a number of bonds, $\bar{l}$ is the mean value of the bond lengths, k is a constant. Degree of aromaticity is calculated excluding bonds C1-C17 and C14-C17. Calculations using this equation indicate that compounds I, II and B are aromatic. The thieno

ring in I has an even higher degree of aromaticity than thiophene. The chemical properties of polycyclic systems containing five-membered heterocyclic rings show that aromaticity of the condensed system can be higher than in isolated ring⁶¹.

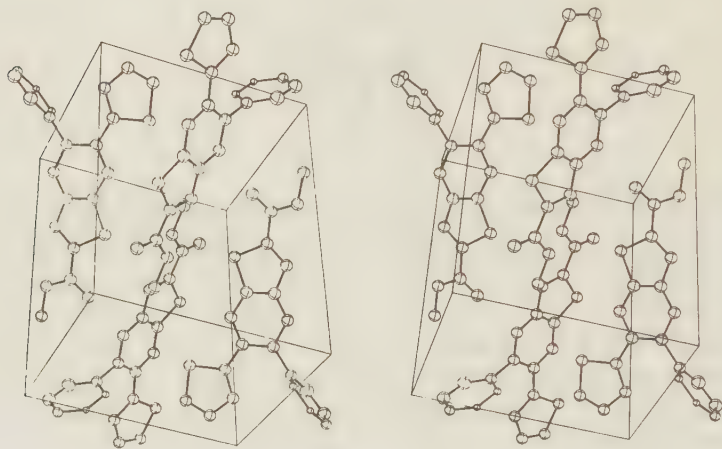


Fig.19. A stereoscopic view of the molecular packing of compound VIII. There are no intermolecular distances smaller than the sum of the van der Waals radii.

3.5 The crystal packing

All compounds in this study are discrete molecules. They show a broad spectrum of packing arrangements with molecules in two sets of planes at a right angle (I), with parallel columns (II), with chains of hydrogen-bonded molecules (III, IV and VI) and a complicated three-dimensional network (V).

Stereoscopic views of the packing arrangement of the molecules in compounds I-VIII are shown in Figures 12-19. In compounds I, II, VII and VIII the packing is determined by van der Waals forces. In compounds III-VI there are also hydrogen bonds between molecules. The molecules in III, IV and VI are held together directly by $N-H \cdots O$ bonds. They form two infinite chains parallel to one of the crystallographic axes. Molecules in the two chains are related by a centre of symmetry.

In compound V, Figure 17, the molecules are held together by hydrogen bonds through water molecules and form a three-dimensional network. The water oxygen is tetrahedrally coordinated with both electron lone-pairs engaged in hydrogen bonds.

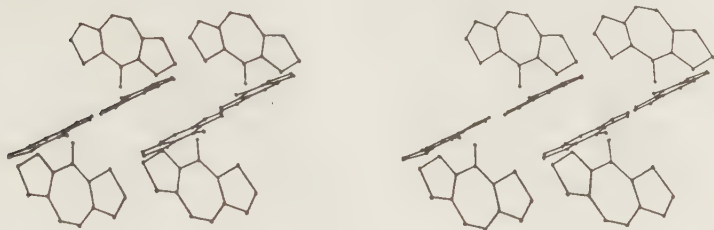


Fig. 12. A stereoscopic view of the crystal packing of compound I. The structure consists of stacked near planar molecules lying in two sets of planes at right angles. The spacing between stacking planes is about 3.4 Å, as in many other aromatic organic compounds. There are no intermolecular distances smaller than the sum of the van der Waals radii.

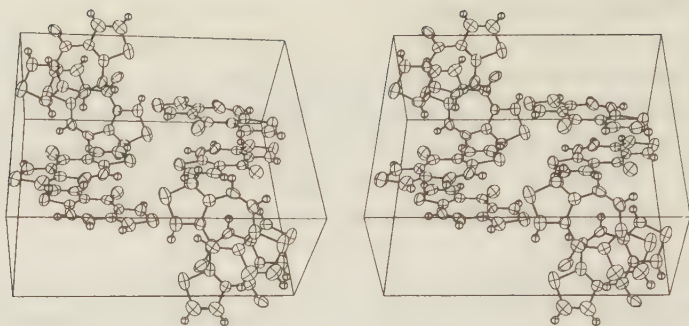


Fig. 13. The crystal packing of compound II. Here, the molecules are stacked in parallel columns. Adjacent molecules in the columns are partially overlapped and strongly twisted relative to each other. Probably the extra bulk of the sulphur atoms prevents more effective stacking. The packing can also be described as a set of sheets with complicated pleating.

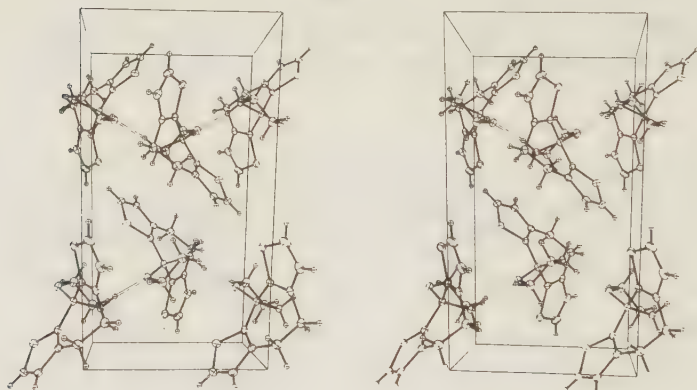


Fig. 14. The crystal packing of compound III. Hydrogen bonds are marked with double lines. There are two conformers in the crystal with alternative arrangements of the dimethylene bridge in the seven-membered ring. The packing appears to be determined primarily by hydrogen bonds ($N-H \cdots O$) between molecules.

These give continuous chains through the crystal.

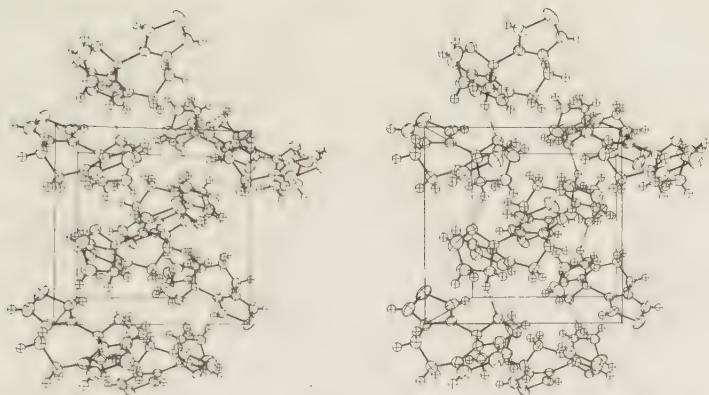


Fig.15. The crystal packing of compound IV. Hydrogen bonds are marked with double lines. The packing here is similar to that of the previous structure. There are two conformers. Molecules of the same conformation are linked together by chains of hydrogen bonds running through the crystal parallel to the b-axis.

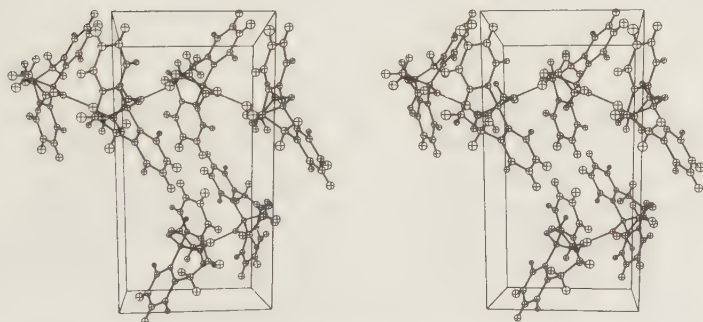


Fig.16. The crystal packing of compound VI. Hydrogen bonds are marked with double lines. The packing here is similar to that of structure III. There are two conformers. The structure appears to be determined by the hydrogen-bonded chains through oxazaborolidine rings parallel to the b-axis. The two benzo rings of adjacent molecules of opposite conformation are parallel but overlapping appears to be poor.

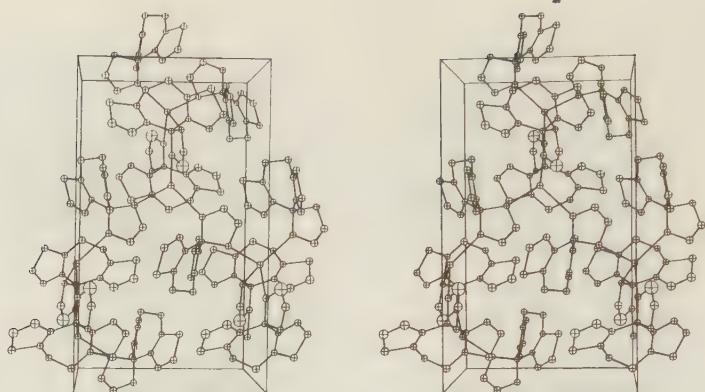


Fig.17. The crystal packing of compound V. Hydrogen bonds are marked with double lines. There are two types of molecules in the structure. There is only one type of dimethylene conformer in this structure, in agreement with the non-centrosymmetric space group, but two different conformations of the tricyclic ring system. The organic molecules are connected through hydrogen bonds from N and O to water, forming an infinite three-dimensional network.

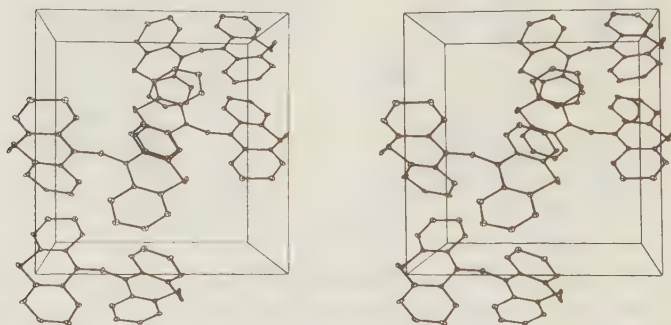


Fig.18. A stereoscopic view of the molecular packing of compound VII. There are no intermolecular distances smaller than the sum of the van der Waals radii.

3.6 Intermolecular contacts and packing efficiency

As can be seen from the account above, compounds I, II, VII and VIII are held together only by van der Waals forces. In these structures no intermolecular distances shorter than the sum of the van der Waals radii were observed other than those involved in the hydrogen bonding. Compounds III-VI have hydrogen bonds and these apparently determine the packing.

A few general remarks can be made here. Belsky and Zorky^{65,66}, on the basis of about 5000 organic compounds investigated up to 1975, showed that organic compounds usually crystallise in the low symmetry crystal systems: 56 % belong to monoclinic, 31 % to orthorhombic and 10 % to triclinic systems. The most common space groups are $P2_1/c$ (38 %) and $P2_12_12_1$ (17 %). The packing of close-packed layers of molecules is most effective with a monoclinic translation at an arbitrary angle to the layer or with inversion centers, glide planes and screw axes as was shown by Kitaigorodsky⁶⁷ who demonstrated that for molecules without inner symmetry elements the closest packing is attainable in the space groups $P\bar{1}$, $P2_1$, $P2_1/c$, Pca , $P2_1/2_1/2_1$, $Pbca$, Pna .

All of the compounds investigated here crystallise in one or other of these space groups. According to Kitaigorodsky (ibid) the majority of organic crystal structures have packing coefficients in the range between 0.65 and 0.77. The table below shows the packing coefficients for the structures investigated here. They fall within this range. These values are of the same order as close packing coefficients for spheres (0.74).

Molecular packing

	I	II	III	IV	V	VI	VII
A	172.8	172.8	221.1	221.1	221.1	259.1	395.2
B	233.5	236.5	318.2	311.5	327.8	335.7	532.2
A:B	.74	.73	.695	.711	.676	.72	.743

A - apparent volume/molecule with Bondi's⁶⁸ and Kitaigorodsky's increments. $B = \frac{V}{z}$, where v =cell volume, z =number of molecules in the unit cell.

3.7 Hydrogen bonding

A hydrogen bond is present when a hydrogen atom is bonded to two atoms⁶⁹ at the same time. It involves a normal covalent bond to one of the atoms, a donor atom D, and a second, weaker, interaction to the other atom, the acceptor atom A, as shown:



The distance D-H is called the donor distance (d), $H\cdots A$ is the acceptor distance (a), $D\cdots A$ the hydrogen bond length (R) and θ is the hydrogen bond angle $D-H\cdots A$. It is usually accepted that a hydrogen bond is present when the acceptor - hydrogen distance is shorter than the sum of the van der Waals radii of H and A. The most frequently used value of $r(O)$ is 1.4 Å, given by Pauling⁷⁰, and for $r(H)$ 1.0 Å as suggested by Baur⁷¹. A geometrical criterion for a hydrogen bond $O\cdots H-O$ is thus an acceptor distance $O\cdots H$ shorter than 2.4 Å.

In the structures studied here there are hydrogen bonds between nitrogen and oxygen (III-V) where nitrogen is donor and oxygen acceptor. These hydrogen bonds are non-linear, with θ values varying between 162° and 167° . These θ values are in agreement with the highest frequency θ interval of $165-170^\circ$ in data from neutron diffraction given by Ferraris & Franchini-Angela⁷². Kroon et al⁷³ have constructed a histogram from a series of 196 values for hydrogen bond angles in polyalcohols and related ROH compounds. These give a maximum in the θ interval $160-165^\circ$. The empirical distribution does not agree well with theoretical calculations which indicate that, at least for $O-H\cdots O$ hydrogen bonds, the configuration of minimum energy should involve a linear hydrogen bond ($\theta = 180^\circ$; Hanskins et al⁷⁴). The geometry of the hydrogen bonds and the water molecules in the structures studied are summarized in the table below. Struc-

ture V contains a water molecule which acts both as acceptor and donor linking four organic molecules through hydrogens and lone electron pairs. This elegant arrangement gives approximately tetrahedral coordination around the water oxygen. Hydrogen bonds go to nitrogen and oxygen atoms from different molecules and thus give an extended three-dimensional network.

Geometry of the hydrogen bonds

Compound	A-H (Å)	O...D (Å)	H...D (Å)	<D-H...O (°)	Donor	Acceptor
III	.93	2.78	1.88	167	N	O
IV	.90	2.91	1.99	165	N	O
VI	.93	2.81	1.99	162	N	O
Va	1.00	2.85	1.97	145	N1	O3
Vb	1.00	2.94	1.97	161	N2	O3
Va	1.00	2.73	1.91	137	O3	O1
Vb	1.00	2.73	1.91	137	O3	O2

From bond-valence analysis of the repulsion between the O atoms in O-H...O hydrogen bonds Brown⁷⁵ has suggested that hydrogen bonds shorter than 2.7 Å are strong, involve strain and are linear, while those longer than 2.7 Å are weak and generally bent.

The O-H...O and N-H...O hydrogen bonds in the structures investigated are of intermediate strength, with O...N or O...O distances of 2.74-2.94 Å and acceptor distances in the range 1.88-1.99 Å. Brown⁷⁵ predicted a correlation between H...O acceptor distances and O-H...O bond angles. His correlation curve between acceptor distances and bond angles is included in Fig. 20 together with corresponding points for the compounds investigated here. The hydrogen bonds in the present compounds show good general agreement with the correlation curve.

Water molecules are present in only one of the structures investigated, structure V. Fig. 21 shows the water molecule with lone pair orbitals and hydrogen bonds to surrounding atoms.

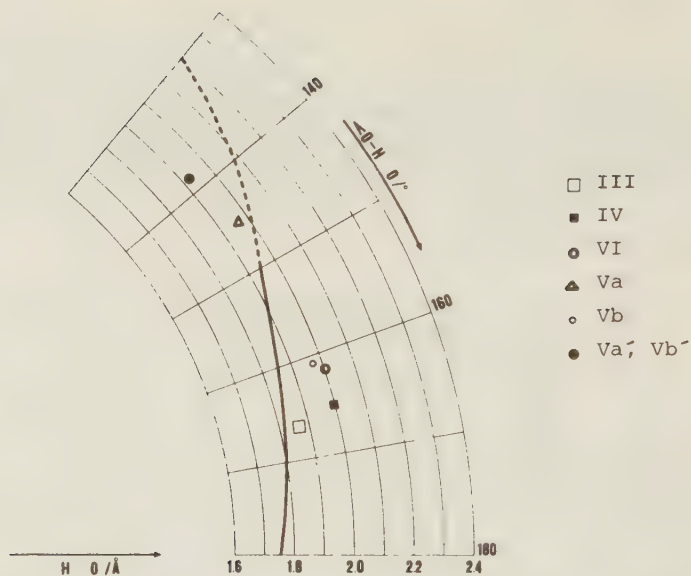


Fig. 20. The correlation between the $O \cdots H$ acceptor distances and $O-H \cdots O$ bond angles in the hydrates. The correlation curve is that predicted by Brown.

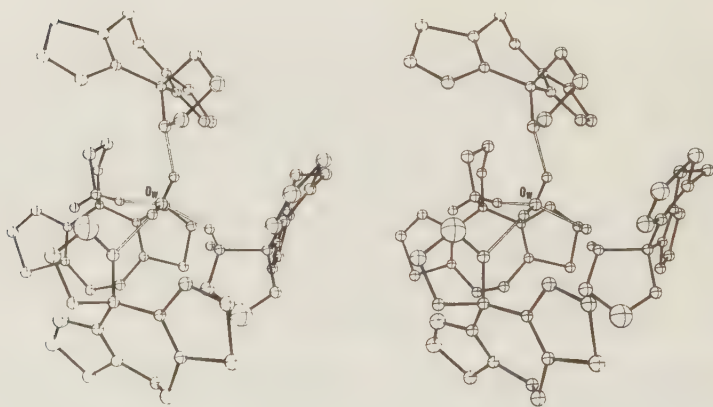
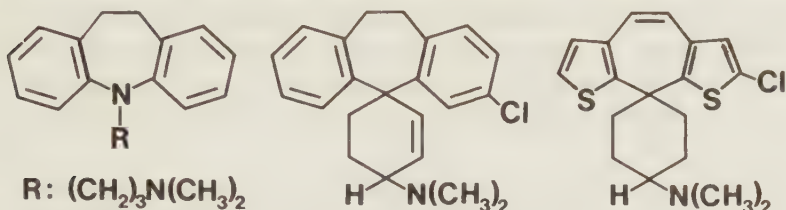


Fig. 21. Hydrogen bonding to the water molecule in the crystal structure of compound V

3.8 Pharmacological aspects

The compounds studied here were originally synthesised for examination of their pharmacological properties. A number of important antidepressants and neuroleptics are of similar type e.g. imipramine⁵³ (P), and compound R, recently studied crystal-



lographically by Wagner⁵⁵ and pharmacologically by Ramsby⁷⁶. The angle between side-rings α , the position of the charged N atom and the distance between the N atom and the fused ring system are important parameters for activity. Variations in these factors, replacement of benzene by another annellated ring, and the effect of type of annellation can have some influence on the biological activity and selectivity. Of the present compounds, the two dithiophenotropones I and II are quite flat and their analogues appear therefore to be unsuitable for activity. Results from pharmacological tests (Gronowitz et al⁷⁷) confirm that thiophene containing rigid spiroamines do not possess biological activity. The dithieno compounds with boron in a seven-membered central ring are angled like the biologically active tricyclic compounds, and therefore have potential interest. Cyclisation of the spiro ring means however that a further charged nitrogen would be required for activity.

The hetero atom in the seven-membered ring can be replaced by other atoms and analogues are known with nitrogen⁵³, germanium⁷⁸, silicon⁷⁹ and sulphur. These offer further possibilities for the variation of the basic structure.

4 SUMMARY

Crystal structures have been determined by X-ray diffraction for some fused tricyclic ring systems containing a central seven-membered ring, either tropone or borepin, and benzene or thiophene side rings.

Two of the substances studied have three-coordinated boron with a planar arrangement; four have tetrahedrally coordinated boron. The B-C bond length is shorter for three-coordinated boron (1.56 Å) than for four-coordinated boron (1.61 Å).

The compounds with four-coordinated boron have a spiro oxazaborolidine ring. In these, the tricyclic ring system usually has a marked dihedral angle. In compound V the crystal has two conformers of the tricyclic ring, one of these is nearly planar. The dimethylene bridge in the borepin ring can have two conformations. In compound III, IV and VI both conformers are present in the crystal. The oxazaborolidine ring is rather unusual. It has a twist conformation. The B-N bond length is 1.64 Å, which corresponds to a normal single bond.

Two of the compounds are dithienotropones. They were found to be planar regardless of type of annellation. This is in contrast to the dibenzo analogues in which the side rings are set at a marked dihedral angle. The dithienotropone ring system has aromatic character, as shown by calculation of degree of aromaticity and polarisation of the carbonyl group.

The thiophene rings are planar in all compounds studied. The annellating bonds in the seven-membered ring have lengths in accordance with their position in the thiophene ring. The bond lengths in the thiophene ring are also affected by the type of annellation. Thus the C-S bond, when connected to the seven-membered ring, is longer (1.73 Å) than a free C-S bonds (1.68 Å).

In three cases the molecules are linked in chains by hydrogen bonds ($O \cdots H-N$) between oxazaborolidine rings and in one structure (V) the molecules are linked through water molecules to a three-dimensional network.

Low temperature collection gives data of significantly higher quality. It was found that isotropic refinement of low temperature data gives results as good as those from anisotropic refinement.

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